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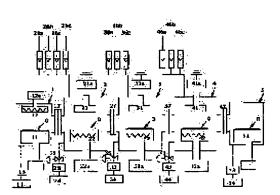


(57)Abstract:

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PROBLEM TO BE SOLVED: To improve the open terminal voltage and a curve factor and to hence improve the conversion efficiency of a solar cell by setting the supply amount of atomic hydrogen to a first thick substantially intrinsic amorphous silicon thin film to a specific range value.

SOLUTION: Hydrogen is supplied, pressure is controlled, and a film growth is similarly regulated to 150Torr. RF is discharged. The RF output density at this time is 0.64W/cm2. It is exposed with hydrogen plasma for a predetermined time, again discharge is stopped, the flow of hydrogen gas is stopped, and evacuated in vacuum until it reaches 10-6Torr or less similarly to that at the time of finishing the film growing step. The series of the steps are repeated, this operation is repeated until a predetermined film thickness is obtained. The film characteristics are largely varied according to the supply amount of atomic hydrogen. The supply amount of the atomic hydrogen for effecting the reduction of defect density is 1×1015 pieces/cm2 to 5×1015 pieces/cm2. Thus, the quality of the amorphous silicon thin film can be enhanced.



## **LEGAL STATUS**

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#### **CLAIMS**

## [Claim(s)]

[Claim 1] The 1st conductive thin film formed on the 1st electrode formed on the substrate, The 1st thin intrinsic semi-conductor thin film, the amorphous silicon thin film of genuineness [ target / thick / 1st / real ], The 2nd conductive thin film, the 3rd conductive thin film, the 2nd thin intrinsic semi-conductor thin film, the 2nd is thick -- substantial -- an intrinsic amorphous silicon thin film and the 4th conductive thin film -- Have the configuration formed in order of the 2nd electrode, and the 1st electrode is transparent. It is the solar battery with which the optical band gap of the 1st thick intrinsic amorphous silicon thin film has a configuration larger than the optical band gap of the 2nd thick intrinsic amorphous silicon thin film. In the solar battery whose optical band gaps of the 1st thick intrinsic amorphous silicon thin film are 1.83eV or more and 1.95eV or less this -- this -- with the formation process of the amorphous silicon semi-conductor thin film which becomes with the 1st thick using hydrogenation silicon compound gas substantially chemistry [ formation / of an intrinsic amorphous silicon thin film ] gaseous-phase vacuum deposition In the process which exposes this thin film by the plasma which is performed by repeating the process which exposes this thin film by the plasma which consists of hydrogen gas, and consists of this hydrogen gas this -- the 1st is thick -- substantial -- the amount of supply of the atomic hydrogen to an intrinsic amorphous silicon thin film -- 1x1015 piece/cm2 the above -- 5x1015 piece/cm2 Amorphous solar battery characterized by being the following.

[Claim 2] The solar battery according to claim 1 with which thickness of an intrinsic amorphous silicon thin film is substantially characterized by the 1st thick 100nm or more thing been 300nm or less.

[Claim 3] The amorphous solar battery according to claim 1 or 2 using the thin film material gas containing hydrogen or inert gas.

[Claim 4] An amorphous solar battery given in any of claims 1-3 characterized by the 1st thick thing which becomes with chemistry gaseous-phase vacuum deposition, and which the bound water quantum of an intrinsic amorphous silicon semi-conductor thin film includes more than below 25 atom %15 atom % substantially they are.

[Claim 5] The amorphous solar battery given in any of claims 1-4 they are with which thickness of an intrinsic amorphous silicon thin film is substantially characterized by the 1st thick 1nm or more thing been 6nm or less formed at 1 time of the membrane formation process which becomes with chemistry gaseous-phase vacuum deposition.

[Claim 6] The amorphous solar battery given in any of claims 1-5 they are with which this chemistry gaseousphase vacuum deposition is characterized by being an optical CVD method, a heat CVD method, a plasma en hunger strike CVD method, a laser en hunger strike CVD method, or a reactant spatter.

[Claim 7] this hydrogenation silicon compound -- SiH4 and Si2H6 from -- amorphous solar battery given in any of claims 1-6 characterized by becoming they are.

[Claim 8] An amorphous solar battery given in any of claims 3-6 characterized by this inert gas being the rare gas chosen from helium, Ne, Ar, Kr, and Xe they are.

[Claim 9] The amorphous solar battery of a publication given in any of claim 1 characterized by for the 1st conductive thin film and the 3rd conductive thin film being semi-conductor thin films of p mold, and the 2nd conductive thin film and the 4th conductive thin film being semi-conductor thin films of n mold - claim 8 they are.

[Claim 10] An amorphous solar battery given in any of claim 1 characterized by for the 1st conductive thin film and the 3rd conductive thin film being semi-conductor thin films of n mold, and the 2nd conductive thin film

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and the 4th conductive thin film being semi-conductor thin films of p mold - claim 8 they are.

[Translation done.]

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## **DETAILED DESCRIPTION**

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to high performance-ization of an amorphous solar battery. [0002]

[Description of the Prior Art] The amorphous silicon solar cell is already put in practical use as an energy source of supply with a small output for driving the ventilating fan of a calculator, a clock, and an automobile. however, a photovoltaics application -- like -- 10W -- as an energy source of supply with the above large outputs -- the generation-of-electrical-energy engine performance and stability -- being related -- enough -- \*\* -- it is in the condition that it cannot say. Therefore, they are the greatest requirements to which generating cost reduction-ization very important as an element of energy supply was not fully attained, but this has barred spread as an object for the power of an amorphous silicon solar cell.

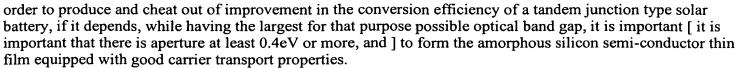
[0003] The membrane formation approach by the plasma CVD which used hydrogenation metallic compounds, such as a silane, is usually used for manufacture of an amorphous solar battery. This forms a thin film on the base installed in the vacuum chamber for membrane formation, and has the advantage which can form membranes to homogeneity to a large area while passing it to the vacuum chamber for membrane formation which controlled hydrogenation metallic compounds, such as a silane, to pressure 10mTorr - 1Torr and it produces and cheats out of decomposition with the plasma. Moreover, since formation of thin films, such as amorphous silicon which has an optical property with a high absorption coefficient to sunlight, is performed by this approach, to that with which there is little required thickness and it can be managed, it can be said that it is the optimal membrane formation approach.

[0004] In addition, since the laminating thin film which consists of what has different optical property and an electrical property can similarly be performed by the same membrane formation technique of plasma CVD, forming in preparation is possible by changing a type of gas and membrane formation conditions. Moreover, forming continuously is also possible by arranging equipment equipped with the same vacuum chamber for membrane formation to a serial.

[0005] the semi-conductor thin film of 1st p mold formed in the configuration of an amorphous solar battery from this on the 1st electrode formed on the base, the 1st thin intrinsic semi-conductor thin film, and the 1st are thick -- substantially with an intrinsic semi-conductor thin film and the semi-conductor thin film of 1st n mold From the single junction type thing which has the configuration which consists of the 2nd electrode, further between the semi-conductor thin film of 1st n mold, and the 2nd electrode There are also a semi-conductor thin film of 2nd p mold, the 2nd thin intrinsic semi-conductor thin film, and the 2nd thick tandem junction type thing that made the intrinsic semi-conductor thin film and the semi-conductor thin film of 2nd n mold constitute substantially.

[0006] About this tandem junction type of thing, an intrinsic semi-conductor thin film and the thicker one of the 2nd where the optical band gaps of an intrinsic semi-conductor thin film differ substantially are substantially desirable from the 1st thick viewpoint of a deployment of exposure sunlight. However, in formation of the amorphous semiconductor thin film by the plasma-CVD method, the band gap range which can form the thin film of high quality is restricted, in the case of an amorphous silicon semi-conductor thin film, it is the range of 1.7 to 1.8eV, and, in the case of an amorphous silicon germanium semiconductor thin film, it is admitted in the optical band gap range narrower than 1.5eV that the membraneous quality deteriorates rapidly.

[0007] A deer is carried out and it is K.M.Mitchell, Solar Cell, and 21 (1987) 127. As shown in drawing 1, in



[0008] Although the membrane formation by plasma CVD is the technique excellent in formation of an amorphous silicon thin film, what accounts for a big role is hydrogen contained in the film as a factor which determines the engine performance of these thin films. And according to the content and joint gestalt in the film of this hydrogen, while that optical band gap is influenced greatly, it has big effect on the transport properties of a carrier. It is greatly dependent on the amount of content hydrogen in the film, it sets to an amorphous silicon semi-conductor thin film, and especially an optical band gap is the bound-water quantum CH in the film. (%) Optical band gap Eopt It turns out that there is the following relation to (eV).

Eopt (eV) =1.60+0.012xCH therefore, the direction which increases the bound water quantum in order to obtain the amorphous silicon semi-conductor thin film which has a large optical band gap -- \*\*\*\* -- going is important.

[0009] especially, optical -- the approach by hydrogen dilution has been taken about the amorphous silicon thin film beyond band gap 1.8eV until now. Consequently, what has an optical band gap high about 0.6eV as compared with the film near [ conventional ] 1.77eV was obtained, and as a result of having applied the obtained film to the amorphous solar battery, what obtains a high open end electrical potential difference was able to be obtained. However, in order to obtain a still higher open end electrical potential difference, it is required to obtain the film which has a higher optical band gap. Furthermore, in order to obtain the solar battery which has a high curvilinear factor, it is desired for the defect density of these film to be also low. Moreover, although it was known that existence of the hydrogen in the film is bearing the big role to reduction of defect density, it was actual that the amount of hydrogen itself which means reduction of defect density was not controllable. Therefore, it was an important old technical problem to control a defect not only including the hydrogen content in the film but a hydrogen bond gestalt.

[Problem(s) to be Solved by the Invention] this invention uses for an intrinsic optical barrier layer the amorphous silicon semi-conductor thin film which was formed by controlling directly the hydrogen content and hydrogen bond gestalt in the film and which an optical band gap is large and reduced defect density with chemistry gaseous-phase vacuum deposition in view of this problem -- especially, the thing for which an open end electrical potential difference and a curvilinear factor are raised, as a result the conversion efficiency of a solar battery is raised -- it aims at things.

[Means for Solving the Problem] This invention is specified according to the following matter.

(1) The 1st conductive thin film formed on the 1st electrode formed on the substrate, The 1st thin intrinsic semi-conductor thin film, the amorphous silicon thin film of genuineness [ target / thick / 1st / real ], The 2nd conductive thin film, the 3rd conductive thin film, the 2nd thin intrinsic semi-conductor thin film, the 2nd is thick -- substantial -- an intrinsic amorphous silicon thin film and the 4th conductive thin film -- Have the configuration formed in order of the 2nd electrode, and the 1st electrode is transparent. It is the solar battery with which the optical band gap of the 1st thick intrinsic amorphous silicon thin film has a configuration larger than the optical band gap of the 2nd thick intrinsic amorphous silicon thin film. In the solar battery whose optical band gaps of the 1st thick intrinsic amorphous silicon thin film are 1.83eV or more and 1.95eV or less this -- this -- with the formation process of the amorphous silicon semi-conductor thin film which becomes with the 1st thick using hydrogenation silicon compound gas substantially chemistry [ formation / of an intrinsic amorphous silicon thin film ] gaseous-phase vacuum deposition In the process which exposes this thin film by the plasma which is performed by repeating the process which exposes this thin film by the plasma which consists of hydrogen gas, and consists of this hydrogen gas this -- the 1st is thick -- substantial -- the amount of supply of the atomic hydrogen to an intrinsic amorphous silicon thin film -- 1x1015 piece/cm2 the above -- 5x1015 piece/cm2 Amorphous solar battery characterized by being the following.

(2) the -- one -- being thick -- substantial -- genuineness -- amorphous -- silicon -- a thin film -- thickness -- 100 -- nm -- more than -- 300 -- nm -- less than -- it is -- things -- the description -- \*\* -- carrying out -- (-- one --) -- a publication -- a solar battery.

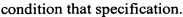
[0011]

- (3) An amorphous solar battery (1) using the thin film material gas containing hydrogen or inert gas, or given in (2).
- (4) chemistry -- a gaseous phase -- vacuum deposition -- becoming -- the -- one -- being thick -- substantial -- genuineness -- amorphous -- silicon -- a semi-conductor -- a thin film -- bound water -- a quantum -- 25 -- atoms -- % -- the following -- 15 -- an atom -- % -- the above -- containing -- things -- the description -- \*\* -- carrying out -- (-- one --) (-- three --) -- any -- or -- a publication -- amorphous -- a solar battery.
- (5) chemistry -- a gaseous phase -- vacuum deposition -- becoming -- one -- a time -- membrane formation -- a process -- forming -- having -- the -- one -- being thick -- substantial -- genuineness -- amorphous -- silicon -- a thin film -- thickness -- one -- nm -- more than -- six -- nm -- less than -- it is -- things -- the description -- \*\* -- carrying out -- (-- one --) (-- four --) -- any -- or -- a publication -- amorphous -- a solar battery.
- (6) The amorphous solar battery given in any of (1) (5) they are with which this chemistry gaseous-phase vacuum deposition is characterized by being an optical CVD method, a heat CVD method, a plasma en hunger strike CVD method, a laser en hunger strike CVD method, or a reactant spatter.
- (7) this hydrogenation silicon compound -- SiH4 and Si2H6 from -- amorphous solar battery given in any of (1) (6) characterized by becoming they are.
- (8) An amorphous solar battery given in any of (3) (6) characterized by this inert gas being the rare gas chosen from helium, Ne, Ar, Kr, and Xe they are.
- (9) the -- one -- conductivity -- a thin film -- and -- the -- three -- conductivity -- a thin film -- p -- a mold -- a semi-conductor -- a thin film -- it is -- and -- the -- two -- conductivity -- a thin film -- n -- a mold -- a semi-conductor -- a thin film -- it is -- things -- the description -- \*\* -- carrying out -- (-- one --) (-- eight --) -- any -- or -- a publication -- a publication -- amorphous -- a solar battery.
- (10) the -- one -- conductivity -- a thin film -- and -- the -- three -- conductivity -- a thin film -- n -- a mold -- a semi-conductor -- a thin film -- it is -- and -- the -- two -- conductivity -- a thin film -- p -- a mold -- a semi-conductor -- a thin film -- it is -- things -- the description -- \*\* -- carrying out -- (-- one --) (-- eight --) -- any -- or -- a publication -- amorphous -- a solar battery . [0012]

[Embodiment of the Invention] first, <u>drawing 1</u> of the 1st is thick for explaining an accompanying drawing -the result of the theoretical conversion efficiency of the optical band gap of an intrinsic amorphous silicon thin
film and the 2nd thick two-layer tandem-die solar battery substantially obtained combining the optical band gap
of an intrinsic amorphous silicon thin film is shown substantially. <u>Drawing 2</u> is the configuration of the solar
battery of this indication. <u>Drawing 3</u> shows change of the amount of supply of atomic hydrogen, conductivity,
and photosensitivity. <u>Drawing 4</u> plots the diffusion coefficient of the hydrogen atom in an amorphous silicon
thin film. <u>Drawing 5</u> is membrane formation equipment used for invention of this indication. <u>Drawing 6</u> shows
the variation of joint hydrogen, and the relation of defect density. <u>drawing 7</u> compared with the open end
electrical potential difference of the solar battery formed by the approach of this indication, and the property of
the solar battery which formed the property of a curvilinear factor by the hydrogen dilution forming-membranes
method -- it is. <u>Drawing 8</u> shows the atomic hydrogen amount of supply in an example 1, and the relation of
defect density. <u>Drawing 9</u> is the schematic diagram of EB vacuum evaporationo machine used in the example 2.

[0013] The semi-conductor thin film of 1st p mold formed on the 1st electrode formed on the base as the fundamental configuration of the solar battery of this invention was shown in <u>drawing 2</u>, The 1st thin intrinsic semi-conductor thin film, the amorphous silicon thin film of genuineness [ target / thick / 1st / real ], It has the semi-conductor thin film of 1st n mold, the semi-conductor thin film of 2nd p mold, the 2nd thin intrinsic semi-conductor thin film, and the 2nd thick configuration substantially formed in order of an intrinsic semi-conductor thin film, the semi-conductor thin film of 2nd n mold, and the 2nd electrode.

[0014] The chief aim is put on this basic configuration having a high open end electrical potential difference, and forming a solar battery with high conversion efficiency highly [ a curvilinear factor ] as a result. And for this purpose The process which forms predetermined thickness with the chemistry gaseous-phase vacuum deposition using hydrogenation silicon compound gas which contains hydrogen or inert gas preferably independently for the purpose of attaining quality improvement of an optical barrier layer, It performs repeating the process which becomes by putting the formed amorphous silicon thin film to the hydrogen plasma on



[0015] The polyimide of the transparence which is glass and high heat resistant resin is used for the base in the solar battery by this invention. It is desirable that it is the transparence electric conduction [ which is transparent and shows the low resistivity of 1x10 to 3 or less ohm-cm ] film which crosses to the large range from 350nm to 1000nm, and has 80% or more of light transmission in the 1st electrode. Specifically, they are an indium stannic acid ghost, zinc oxides, and these laminated-structure thin films.

[0016] As for the temperature which the semi-conductor thin film which constitutes the solar battery by this invention is performed by chemistry gaseous-phase vacuum deposition, such as a plasma-CVD method, an optical CVD method, and a reactant spatter, and is formed, it is desirable that it is [ 300 degree-C or less ] 100 degrees C or more. It is 250 degrees C or less 150 degrees C or more still more preferably. A limit of such temperature is added in order to stop the thermal damage given to the 1st electrode used as a substrate as much as possible.

[0017] Usually, SiH4 and Si2H6 which are hydrogenation silicon compound gas which is material gas by the plasma-CVD method These chlorination compounds or a fluorine substituted compound is supplied with hydrogen gas and rare gas if needed. Furthermore, the hydride gas which contains carbon if needed is also supplied. In order to form the semi-conductor thin film of p mold according to a conventional method, potassium-borohydride compound gas is used, and in order to form the semi-conductor thin film of n mold, hydrogenation phosphorus compound gas and arsine compound gas are used.

[0018] The pressure at the time of being formed by the plasma-CVD method is performed on the conditions of 1 or less Torr. About the capacity to pass, suiting a predetermined pressure is determined timely.

[0019] Boron is intentionally mixed in the semi-conductor thin film of 1st p mold, and the semi-conductor thin film of 2nd p mold as an impurity, and the content is 1% or less and 0.5% or more. Consequently, when these p type semiconductor thin films are amorphous, it has 1x10 to 6 or more S-cm the conductivity of 1x10 to 4 or less S-cm, and in being a microcrystal layer, it has the conductivity below 1x10-1 or more S-cm1x101 S-cm. In addition, this p type of semi-conductor thin film has the large optical band gap 1.8eV or more, and an amorphous carbonization silicon semi-conductor thin film is used. And it is desirable still more desirable that it is [5nm or more] 15nm or less, and the thickness of these p type semiconductor thin films is 6nm or more 10nm or less.

[0020] the 1st thin intrinsic semi-conductor thin film and the 2nd thin intrinsic semi-conductor thin film of the 1st p type semiconductor thin film and the 1st are thick -- it has the junction to an intrinsic semi-conductor thin film, electric transport properties and the 2nd p type semiconductor thin film, and a property with being thick 2nd for smoothing the junction to an intrinsic semi-conductor thin film, and electric transport properties substantially substantially. It is desirable still more desirable that it is [5nm or more] 25nm or less, and the thickness of these thin intrinsic semi-conductor thin films is 10nm or more 20nm or less.

[0021] Phosphorus and arsenic are intentionally mixed in the semi-conductor thin film of 1st n mold, and the semi-conductor thin film of 2nd n mold as an impurity, and the content is 1% or less and 0.5% or more. In addition, even if this n type of semi-conductor thin film is amorphous and it is a microcrystal, it is not cared about. Consequently, when these n-type-semiconductor thin films are amorphous, it has 1x10 to 6 or more S-cm the conductivity of 1x10 to 4 or less S-cm, and in being a microcrystal layer, it has the conductivity below 1x10 -1 or more S-cm1x101 S-cm. It is desirable still more desirable that it is [5nm or more] 25nm or less, and the thickness of these n-type-semiconductor thin films is 10nm or more 20nm or less.

[0022] As for an intrinsic semi-conductor thin film, an amorphous silicon semi-conductor thin film and an amorphous silicon germanium semiconductor thin film are used for the 2nd thick real target. SiH4 and Si2H6 which are hydrogenation silicon compound gas as material gas at formation of an amorphous silicon semi-conductor thin film These chlorination compounds or a fluorine substituted compound is supplied with hydrogen gas and rare gas if needed. By the way, the potassium-borohydride compound adjusted to 100 ppm or less by hydrogen dilution may be supplied.

[0023] SiH4 and Si2H6 which are hydrogenation silicon compound gas as material gas at formation of an amorphous silicon germanium semiconductor thin film GeH(s)4 which are germanium hydride compound gas, these chlorination compounds, and a fluorine substituted compound are supplied with hydrogen gas and rare gas if needed. By the way, the potassium-borohydride compound adjusted to 100 ppm or less by hydrogen dilution may be supplied.



[0024] An intrinsic amorphous silicon semi-conductor thin film is substantially formed by the 1st thick procedure shown below. That is, predetermined thickness is formed by the chemistry gaseous-phase vacuum deposition using the independent hydrogenation silicon compound gas which contains hydrogen or inert gas preferably. The chemistry gaseous-phase vacuum deposition used here is an optical CVD method, a plasma en hunger strike CVD method, a reactant spatter, etc.

[0025] SiH4 which is Sin H2m+2 (n and m are one or more integers) at hydrogenation silicon compound gas, and Si two H6 And Si three H8 etc. -- it is mentioned. Moreover, it is also possible to use the compound by which the hydrogen atom was permuted with the chlorine atom or the fluorine atom as an ingredient of these hydrogenation metallic compounds.

[0026] Furthermore, the inert gas used as dilution gas has helium, Ne, Ar, Kr, Xe, etc. like hydrogen. In addition, although it does not regulate especially about the rate of the dilution ratio by these gas, it is usually desirable that it is 30 or less to membrane formation material gas 1 as a volumetric flow rate ratio. In the system containing these gas, from the phase which the process in which an amorphous semiconductor thin film is formed ended, while shifting to the process put to the hydrogen plasma, vacuum suction is performed with chemistry gaseous-phase vacuum deposition. Before going into the process put to the hydrogen plasma after membrane formation process termination by this, effect of a residual of the gas for membrane formation can be made as small as possible.

[0027] On the contrary, since the gas for membrane formation passed in the membrane formation process will both dilute with a lot of hydrogen gas which remains by that residence time when not inserting this vacuum suction between a membrane formation process and the process put to the hydrogen plasma, it becomes easy to produce crystallization. Therefore, the result of having separated from the purpose of manufacture of the amorphous silicon thin film of the target high quality will be brought.

[0028] As for the bound water quantum of the amorphous silicon thin film formed in a membrane formation process, it is desirable that it is more than under 25 atom %15 atom %. when the bound water quantum is under 15 atom %, it already considers as the purpose also by the approach of this invention -- optical -- the thin film beyond band gap 1.85eV cannot be obtained. Therefore, as for the bound water quantum in the film, it is desirable that it is more than 15 atom %.

[0029] Moreover, when the bound water quantum is under pentatomic %, in order to form the amorphous silicon semi-conductor thin film, there are two cases shown below. That is, the hydrogen contained in the film is sufficient high temperature to break away and the case where membranes are specifically formed at the substrate temperature of 385 degrees C or more. Moreover, it is the case where that membrane formation is performed in the state of the hydrogen dilution containing the hydrogen of an overlarge, and as a result of the joint gestalt in the film changing [ an amorphous semiconductor thin film ] a lot, and the bound water quantum's being large and falling in this case, it will microcrystal-ize.

[0030] First, when substrate temperature is too high (i.e., when substrate temperature is 385 degrees C or more), it sets like a film formation fault and the balking of hydrogen is strong rather than invasion of hydrogen. Therefore, putting to the hydrogen plasma in membrane formation and these temperature conditions cannot constitute an effective role any longer. Moreover, when producing microcrystal-ization, the bound water quantum in the film will decrease greatly, and will usually become 3 atom % extent, and this will shift from a claim. Since a motion of the hydrogen in the film is restricted, it will become impossible moreover, to expect the structural change by putting to hydrogen PURAZUNA about the film which produced microcrystal-ization. Furthermore, when the bound water quantum in the film exceeds 25 atom %, they are the case where an amorphous semiconductor thin film is formed [ \*\*\*\*\*\* ] for the film with chemistry gaseous-phase vacuum deposition in the state of low temperature which is close to a room temperature, and the case where to drive in hydrogen is needed in the film compulsorily for ion implantation equipment etc.

[0031] In the condition of being close to a room temperature, although it is also possible to form a thin film to which the bound water quantum in the film exceeds 25 atom % according to conditions, it cannot set like a film growth fault and the membrane formation radical for performing film formation cannot fully migrate on a front face. Since a lot of hydrogen has already existed in the film, it will become impossible in this case, to already expect effectiveness like compensation of a defect by making hydrogen invade into the film by putting to the hydrogen plasma. Therefore, as for the bound water quantum in the film of the film formed in the approach of forming the film with the chemistry gaseous-phase vacuum deposition using the hydrogenation metallic-



compounds gas containing hydrogen or inert gas, it is desirable that it is more than under 25 atom %15 atom %. [0032] Therefore, when forming an amorphous silicon thin film, the membrane formation temperature requirement for which are suitable is limited. In order for the bound water quantum in the film of the amorphous semiconductor formed with chemistry gaseous-phase vacuum deposition to be more than below 25 atom %15 atom %, it is desirable that the membrane formation temperature requirement is less than 250 degrees C 100 degrees C or more. Furthermore, it is desirable still more desirable that it is [1nm or more] 6nm or less, and the thickness of the thin film formed at 1 time of a membrane formation process by such chemistry gaseous-phase vacuum deposition is 2nm or more 5nm or less.

[0033] When the thickness formed of 1 time of a membrane formation process is not much thin less than 1nm, superfluous hydrogen is supplied into the film, and the amorphous silicon thin film of the high quality made into the purpose cannot be formed.

[0034] Moreover, when the thickness formed of 1 time of a membrane formation process is not much thicker than 6nm, in a process, a result to which osmosis of the atomic hydrogen already supplied is not fully carried out will be brought by putting to the hydrogen plasma. Furthermore, the amount of the atomic hydrogen which occurs during discharge and is supplied to a base front face in the process which exposes this thin film by the plasma which consists of hydrogen gas is 2 1x1015 pieces/cm. It is 2 5x1015 pieces/cm above. It is desirable that it is the following.

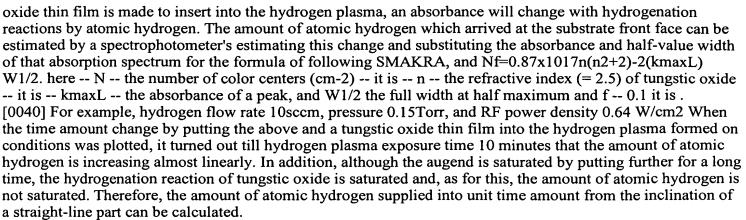
[0035] <u>Drawing 3</u> observes the membranous conductivity and the photosensitivity which were obtained according to the difference in the amount of supply of atomic hydrogen. The amount of supply of atomic hydrogen is 2 1x1015 pieces/cm. In being the following, it turns out that photosensitivity is low. On the other hand, the amount of supply of atomic hydrogen is 2 6x1015 pieces/cm. When many, the rapid increment in the conductivity of an amorphous thin film is checked, and it is judged that crystallization has arisen. [0036] Thus, the important point of this approach is that the amount of supply of atomic hydrogen itself is important. If osmosis of the hydrogen by putting to the hydrogen plasma is performed by diffusion of atomic hydrogen, it should be greatly influenced with membrane formation temperature. <u>Drawing 4</u> plots the diffusion coefficient of hydrogen measured by W.Beyer J.Appl.Phys.53, 8735 (1982), M.Reinelt J.Non-Cryst.Solid

[0037] The range of the most suitable thin film formation temperature requirement by this approach is 160 to 200 degrees C, and the diffusion constant of the hydrogen in this range is less than [ more than 2x10-20cm2/s2x10-18cm2/s]. For example, it is expected that the hydrogen concentration 20 seconds after the surface hydrogen in a location deeper 4nm than a front face since this value is very small becomes very low to surface hydrogen concentration in the case of diffusion constant 2x10-18cm2/s of hydrogen in the suitable temperature requirement in the approach of this indication. Therefore, it is clear that diffusion of hydrogen is not the essential effectiveness of this approach. Then, it is whether to be in the condition that the network of the component with which thinking constitutes membrane structure from a membrane formation front face in a depth of several nm did not fully solidify, but made it confused. The atomic hydrogen given from the membrane formation front face in such a field permeates easily, and is considered whether to have deteriorated membrane structure. Moreover, you may differ from the supply energy density in a membrane formation process, the membrane formation flow and pressure requirement, and RF power density in the process put to the hydrogen plasma and a membrane formation flow and pressure requirement.

[0038] What is necessary is just the conditions for forming the usual amorphous semiconductor in a membrane formation process in this invention. For example, in the case of the membrane formation approach using RF plasma, suitable supply energy density is 0.01 W/cm2. It is 1 W/cm2 above. It is desirable that it is the following and the membrane formation pressure is 10mTorr. It is desirable that it is 1 or less Torr above. Furthermore, it sets at the process put to the hydrogen plasma, and the RF power density is 0.01 W/cm2. It is 1 W/cm2 above. It is desirable that it is the following and the membrane formation pressure is 10mTorr. It is desirable that it is 1 or less Torr above.

[0039] The amount of the atomic hydrogen which occurs during discharge and is supplied to a base front face in the process which exposes this thin film by the plasma which consists of hydrogen gas in this invention is 2 1x1015 pieces/cm. It is 2 5x1015 pieces/cm above. It is desirable that it is the following. Measurement of the amount of atomic hydrogen supplied to a substrate front face is performed as follows. That is, on a glass substrate, electron beam vacuum deposition is used and a tungstic oxide thin film is formed. If this tungstic

59&60, and 169 (1983) as the inverse number of absolute temperature.



[0041] The speed of supply of the atomic hydrogen called for from this straight-line part is RF power density 0.64 W/cm2 which is the above-mentioned conditions. In conditions, 1x1014 pieces [/cm ] 2 / second came. Furthermore, hydrogen flow rate 10sccm, pressure 0.15Torr, and RF power density 0.13 W/cm2 When it put to the hydrogen plasma formed on conditions and asked for the atomic hydrogen speed of supply similarly, 4x1013 pieces [/cm ] 2 / second came.

[0042] Then, if an axis of abscissa is set as the square root of RF power density and an atomic hydrogen speed of supply is plotted, the speed of supply of the atomic hydrogen obtained in two RF power density can be approximated by the straight line which passes through a zero. Thus, the square root of RF power density can determine the atomic hydrogen amount of supply supplied uniquely.

[0043] From this, the amount of the atomic hydrogen supplied is controllable by the RF power density and time amount. for example, the atomic hydrogen to which it is supplied when RF discharge power density for forming the hydrogen plasma is 0.64 W/cm2 -- around for 1 second -- 1x1014 piece/cm2 it is . Therefore, the time amount put to the hydrogen plasma which suits the amount of supply of the atomic hydrogen by the approach of this indication becomes less than 50 seconds 20 seconds or more.

[0044] Next, the basic configuration of the equipment for carrying out this invention is shown in <u>drawing 5</u>. That is, this equipment has five-room composition of the substrate preparation room 1, three membrane formation rooms 2, 3, and 4, and the substrate ejection room 5. And the base preparation room, the membrane formation room, and the substrate preparation room are connected with gate valves 17, 27, 37, and 47, respectively.

[0045] A substrate preparation room is formed with the turbo molecular pump 13 and rotary pump 14 for power-source 12a for supplying power to a heater 12 and its heater, and evacuation in order to heat the base maintenance base 11 for holding a base, and a base. While the substrate installed in substrate preparation by this exhaust air system is heated at a heater, preparations required for membrane formation are made by carrying out evacuation.

[0046] There is an RF electrode 21 in the membrane formation room 2, and discharge is formed between the substrate heating heater 22 tops. The RF electrode 21 is RF generator 21a. Power is impressed. Moreover, a heater 22 is heater power-source 22a. Power is impressed. A substrate 0 is installed on a heater and a heating temperature up is carried out at a heater. Moreover, although evacuation of this membrane formation room 2 is carried out with a turbo molecular pump 23 and a rotary pump 24, the pressure of this membrane formation room has composition whose pressure can be regulated by the conductance bulb 25. The gas for membrane formation is massflow controllers 26a, 26b, 26c, and 26d. It is controlled while the gas by which the flow rate was controlled is supplied.

[0047] In addition, it is the configuration same also about the membrane formation rooms 3 and 4 as the membrane formation room 2. The substrate ejection room 5 is formed with the turbo molecular pump 53 and rotary pump 54 for the base maintenance base 51 for holding a base, and evacuation. After natural radiationnal cooling of the substrate installed in substrate preparation is carried out on a base maintenance base by this exhaust air system, it is taken out outside by it. It is [ the membrane formation rooms 2 3, and 4 ] suitable, and they are used for each class of the solar battery obtained.

[0048] That is, the semi-conductor thin film of 1st p mold, the 1st thick intrinsic semi-conductor thin film, the



semi-conductor thin film of 2nd p mold, and the 2nd thin intrinsic semi-conductor thin film are formed at the membrane formation room 2. An intrinsic semi-conductor thin film is formed in the 1st thick real target at the membrane formation room 3 at an intrinsic amorphous silicon thin film and the 2nd thick real target. And the semi-conductor thin film of 1st n mold and the semi-conductor thin film of 2nd n mold are formed at the membrane formation room 4.

[0049] The important point in this equipment is having RF discharge electrode for forming the hydrogen plasma apart from the device for membrane formation. \*\* which forms the 1st genuineness amorphous silicon thin film in the case of the membrane formation equipment in <u>drawing 5</u> is the membrane formation room 3. When the membrane formation equipment in <u>drawing 5</u> is used, in order to be based on the membrane formation technique using RF discharge electrode also in membrane formation, the process put to a membrane formation process and the hydrogen plasma by the same system can be performed.

[0050] By performing this approach, the bound water quantum which exists in the film tends to increase. While the bound-water quantum in the film increases in connection with this in the case of a hydrogenation amorphous silicon thin film, it is in the inclination which the optical band gap makes large. This is because activity atomic hydrogen is supplied effectively in the film, can supply hydrogen to the uncombined hand in the film without the approach of controlling that generating by the usual membrane formation approach effectively, and can make it reduce defect density greatly as a result by this approach. Drawing 6 compares the change value of the bound water quantum in the film and the degree of reduction of defect density which increase by putting to the 1st hydrogen plasma when forming only an intrinsic amorphous silicon semi-conductor thin film substantially equivalent to the membrane formation room 3 of a configuration of being shown in drawing 5. Consequently, it is admitted that effectiveness is in reduction of defect density more as the case of the increment in the bound water quantum in the film of being large.

[0051] Thus, while making it possible to be able to design the optical band gap of an amorphous thin film freely by controlling directly the hydrogen content and hydrogen bond gestalt in the hydrogen film, quality improvement of the thin film by reduction of a defect can be attained.

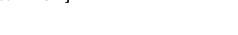
[0052] And the 1st open end electrical potential difference substantially obtained to the optical band gap of a genuineness amorphous silicon thin film and the relation of a curvilinear factor are shown in drawing 7. \*\* forms a genuineness amorphous silicon thin film in the 1st real target among drawing by the 1st approach to form a genuineness amorphous silicon thin film by the hydrogen dilution forming-membranes method substantially, and for O carry out this invention. The open end electrical potential difference which the optical band gap of the film formed by the hydrogen dilution forming-membranes method is 1.83eV or less, therefore is obtained from this is less than [1.81V]. Moreover, although just the curvilinear factor has obtained the high result when the film which has a 1.77eV optical band gap is used, an open end electrical potential difference is low, and it turns out that the following [1.8V] have not been obtained.

[0053] On the other hand, it has the high value to which the high open end electrical potential difference beyond 1.8V is obtained easily substantially in the case of the 1st solar battery using a genuineness amorphous silicon thin film formed using the film formed by the approach for carrying out this invention, and a curvilinear factor also exceeds 0.7. It is admitted that the approach of this indication plays a big role in improvement in an open end electrical potential difference and a curvilinear factor so that the above result may show. Hereafter, an example explains an example of the mode of operation of this invention.

[Example]

(Example 1) The equipment used for formation of a thin film is the same as the equipment shown in <u>drawing 5</u>. Only the intrinsic amorphous silicon thin film was formed in the 1st thick real target in the example 1. As material gas for membrane formation, mono-silane gas was used as it was. The flow rate of mono-silane gas is massflow controller 36a [ in / it is 10sccm(s) and / <u>drawing 5</u> ]. It minds and passes. The membrane formation temperature in this system is 175 degrees C. And although membrane formation was performed so that it might become predetermined thickness, in this example, the thickness per time could be 4nm. Membrane formation is interrupted with termination of RF discharge, and the gas supplied to a chamber is stopped. And vacuum suction is started in the state of main valve open, and it is made 10 to 6 or less Torrs.

[0055] Next, it goes into the process put to the hydrogen plasma. First, while supplying hydrogen, pressure control is performed, and they are 150mTorr(s) as well as membrane formation. It adjusts. In addition, hydrogen



is massflow controller 36b in <u>drawing 5</u>. It minds and passes. And RF is discharged. RF power density at this time -- 0.64 W/cm2 it is . Actuation put to predetermined time amount and the hydrogen plasma was performed, and vacuum suction was performed until it stopped the flow rate of hydrogen gas and was again set to 10 to 6 or less Torrs like the time of membrane formation process termination with a halt of discharge. By repeating these processes of a series of, this actuation was repeated and was performed until it became predetermined thickness (300nm or more).

[0056] <u>Drawing 8</u> uses the above-mentioned result, i.e., the amount of supply of atomic hydrogen, as an axis of abscissa, and shows the situation of a fall of defect density. From this result, it is admitted with the amount of supply of atomic hydrogen that that film property is changing a lot. the discharge power density of RF -- 0.64 W/cm2 it is -- the speeds of supply of the atomic place hydrogen at this time are 1x1014 pieces [/cm] 2 / s. It is admitted as a result of this examination that that film property is changing [ the time amount put to the hydrogen plasma] a lot depending on an increment.

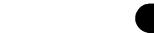
[0057] The defect density in the film is falling as the time amount put to the hydrogen plasma is made to increase. Furthermore, when the time amount put to this hydrogen plasma exceeded 60 seconds, crystallization arose and it was admitted that the remarkable increment in dark conductivity had started. At this time, the amount of supply of atomic hydrogen is 2 6x1015 pieces/cm. It is a time of reaching.

[0058] The amount of supply of the atomic hydrogen which has effectiveness in reduction of defect density from drawing 8 is 2 2x1015 pieces/cm. It is 2 4x1015 pieces/cm above. It turns out that it is the following. As mentioned above, it was checked that quality improvement of an amorphous silicon thin film had been made by the approach of this indication.

[0059] (Example 2) The equipment used for formation of a thin film is the same as the equipment shown in drawing 5. The substrate used for the solar battery on the occasion of formation forms the thin film of tin oxide as the 1st electrode on a glass substrate. The substrate with which this tin oxide was formed is U type substrate by Asahi glass incorporated company, and has 80% or more of light transmission in the light field in 300nm to 800nm, and is 1x10-3 ohm/cm. The thing with the following resistivity was used. The thickness of this tin oxide layer is about 1 micrometer, while evacuation is carried out until a substrate becomes 10 to 6 or less Torrs at a substrate preparation room -- 120 degrees C -- it was heated and was left for 15 minutes. Then, a substrate is conveyed at the membrane formation room 2, and evacuation is carried out so that it may be set to 10 to 6 or less Torrs, this membrane formation room 2 -- setting -- a base -- 150 degrees C -- it is heated. [0060] First, the semi-conductor thin film of 1st p mold is formed. As material gas to be used, they are a mono silane, methane, and 1% diboron hexahydride gas (potassium-borohydride compound) by hydrogen dilution. Each flow rates were mono-silane 4sccm, 1% dilution diboron hexahydride gas 6sccm, and methane flow rate 5sccm, and were membrane formation pressure 150mTorr, RF discharge power-flux-density 0.1 W/cm2, and membrane formation time amount 90 seconds. The base retention temperature at this time is 160 degrees C. Consequently, the semi-conductor thin film of 1st p mold which has about 60 thickness was formed. [0061] Furthermore, the 1st thin intrinsic semi-conductor thin film is formed. As material gas to be used, they are a mono silane, methane, and hydrogen. Each flow rates are mono-silane 6sccm, initial flow rate of methane flow rate 5sccm, amount of termination trend of the world 0sccm, and hydrogen gas 20sccm. Moreover, they were membrane formation pressure 100mTorr, RF discharge power-flux-density 0.1 W/cm2, and membrane formation time amount 300 seconds. The base retention temperature at this time is 160 degrees C. Consequently, the 1st thin intrinsic semi-conductor thin film which has about 120A thickness was formed. [0062] After carrying out evacuation, a substrate is conveyed in the membrane formation room 3, until it stops supply of gas in a substrate and is set to 10 to 6 or less Torrs. A substrate is conveyed in the membrane formation room 3, and an intrinsic amorphous silicon thin film is formed in the 1st thick real target. The

differed and it was set as 200nm in the example 2. [0063] Furthermore, a substrate is conveyed in the membrane formation room 4, and the semi-conductor thin film of 1st n mold is formed. As material gas to be used, they are a mono silane, 0.2% phosphine gas (hydrogenation phosphorus compound) by hydrogen dilution, and hydrogen. Each flow rates were mono-silane 0.5sccm, 0.2% dilution phosphine gas 30sccm, and hydrogen quantity-of-gas-flow 90sccm, and were membrane formation pressure 200mTorr, RF discharge power-flux-density 0.8 W/cm2, and membrane formation time amount 390 seconds. The substrate retention temperature at this time is 160 degrees C. Consequently, the semi-

formation conditions of this thin film are completely the same as an example 1. However, only thickness



conductor thin film of 1st n mold which has about 300A thickness was formed. And a substrate is conveyed again at the membrane formation room 2. At the membrane formation room 2, the semi-conductor thin film of 2nd p mold is formed on the same formation conditions as the semi-conductor thin film of 1st p mold. Furthermore, the 2nd thin intrinsic semi-conductor thin film is formed on the same formation conditions as the 1st thin intrinsic semi-conductor thin film.

[0064] A substrate is conveyed again at the membrane formation room 3, and forms an intrinsic amorphous silicon thin film in the 2nd thick real target. it deals in the conditions for formation with following one, and comes out of them. That is, the flow rate is 10sccm, using a mono silane as material gas to be used. 2 and membrane formation time amount were 2 hours membrane formation pressure 50mTorr and 0.1W [/cm ] RF discharge power flux density. The base retention temperature at this time is 175 degrees C. Consequently, the 2nd thick intrinsic amorphous silicon thin film which has 4000A thickness was obtained.

[0065] Furthermore, the semi-conductor thin film of 2nd n mold is formed. The conditions to form are completely the same as the conditions which form the semi-conductor thin film of 1st n mold.

[0066] Furthermore, the 2nd electrode is formed. The 2nd electrode is constituted by the layer which consists of an oxide of indium tin in the case of an example 2, the layer which consists of silver, and the layer which consists of aluminum. All of these layers were formed with EB vacuum evaporation vessel shown in drawing 9.

[0067] EB vacuum evaporationo machine consists of substrate preparation / ejection room 6, and the membrane formation room 7. At substrate preparation / ejection room 6, after vacuum suction of the substrate carried in the base electrode holder 61 is carried out to 10 to 6 or less Torrs of degree of vacuums, it is conveyed at the membrane formation room 7, and is put on the substrate electrode holder 78 by the transfer rod 62. the place which the substrate conveyed at the membrane formation room 7 was heated by 200 degrees C at the heater 72, and became the conditions of 10 to 6 or less Torrs of degree of vacuums -- electron gun 71a from -- a thin film is formed of the emission from the target heated with the emitted electron.

[0068] Formation is performed in the layer which consists of an oxide of indium tin by the emission by electron ray heating which targets the oxide of indium tin under existence of the oxygen supplied by massflow controller 76a. The thickness of the layer which consists of an oxide of the indium tin at this time is 400A. Furthermore, after cooling at 100 degrees C or less, 2000A of silver thin film layers is formed by irradiating the electron ray of high density at a silver target. It pulls and continues and is the thin film layer of aluminum similarly 1000A It forms.

[0069] Thus, the amorphous solar battery which has the structure specified by this invention can be formed. When the conversion efficiency of this solar battery was measured, the result shown in [Table 1] was obtained. That is, the value of 1.85V with an open end electrical potential difference very high as a solar battery which has an amorphous silicon thin film in an intrinsic layer was acquired. Furthermore, reflecting the goodness of membranous quality, the curvilinear factor was also as high as 0.75, consequently was able to form the efficient solar battery which has 10.5% of conversion efficiency.

[0070] (Example 1 of a comparison) The example 1 of a comparison is explained hereafter. The equipment used for formation of a thin film is the same as the equipment shown in <u>drawing 5</u>. The configuration of the amorphous solar battery in the example 1 of a comparison is completely the same as that of an example 2 on the 1st thick real target except an intrinsic amorphous silicon thin film. Therefore, the manufacture approach is completely the same as that of the 1st real target except an intrinsic thin film. Therefore, in the example 1 of a comparison, the business can be attained 1st by [ thick ] describing only the formation approach of an intrinsic amorphous silicon thin film substantially.

[0071] First, about a base, it is completely the same as that of an example 2. Moreover, it is completely the same as that of the semi-conductor thin film [ of 1st p mold ], and 1st thin things stated in the example 2 also about formation to an intrinsic semi-conductor thin film substantially.

[0072] Membranes were formed by diluting by hydrogen in the example 1 of a comparison in formation of an intrinsic amorphous silicon thin film substantially, using a mono silane as 1st different thick material gas from an example 2 to be used. The flow rate of a mono silane is 10sccm(s), and the flow rate of hydrogen gas is 10sccm(s). 2 and membrane formation time amount were 2 hours membrane formation pressure 50mTorr and 0.1W [/cm] RF discharge power flux density. The base retention temperature at this time is 175 degrees C. Consequently, the intrinsic amorphous silicon thin film was got by the 1st thick real target which has 2000A



thickness. In addition, the optical band gap of this film was 1.83eV as a result of forming using the single film formed in the same approach.

[0073] It is completely the same as that of the case of an example 2 also about the formation approach about the 2nd electrode. Thus, the solar battery was formed. When the conversion efficiency of this solar battery was measured, the result shown in Table 2 was obtained. That is, the open end electrical potential difference was 1.80V, the curvilinear factor was 0.70 consequently, and conversion efficiency was 10.1%. A result is shown in [Table 2].

[0074] Hereafter, in the example 1, mono-silane gas and mono-germane gas were used as material gas for membrane formation. The flow rate of mono-silane gas was 5sccm(s), and the flow rate of mono-germane gas is the purpose which forms the thing of different optical band GYA@PPU, and changed the flow rate condition. In this example, a sink and mono-silane gas passed 5sccm(s) through the massflow controller 72 through the massflow controller [ in / in mono-germane gas / drawing 3 ] 71 by the flow rate of 1sccm. the used membrane formation conditions -- as substrate temperature -- 175 degrees C -- it is -- the membrane formation pressure -- 150mTorr(s) it was . RF power density -- 0.04 W/cm2 it is .

[0075] The configuration of the equipment used in an example is the same configuration as the equipment shown in drawing 3. Consequently, the membrane formation rate of the film formed using mono-silane gas and mono-germane gas as obtained material gas for membrane formation was 0.2A/s or less. Consequently, the photoconductivity of the film formed in the example was higher than the film obtained by hydrogen dilution membrane formation, and dark conductivity was low generally, and it was confirmed that it is the thin film which has good photosensitivity. The axis of abscissa was set as the amount of supply of atomic hydrogen for this, and drawing 8 showed the situation of a fall of conductivity and photosensitivity. From this result, it is admitted with the amount of supply of atomic hydrogen that that film property is changing a lot.

[0076] The amount of supply of the atomic hydrogen which has effectiveness in reduction of defect density from drawing 8 is 2 2x1015 pieces/cm. It is 2 4x1015 pieces/cm above. It turns out that it is the following. As mentioned above, it was checked that quality improvement of an amorphous silicon thin film, as a result an

amorphous silicon thin film solar cell had been made by the approach of this indication.

[0077]

x ID=000003			
[0078]	<del></del>	······································	
[0078] [Table 2]			
x   ID=000004			

[0079]

[Table 1]

[Effect of the Invention] While making it possible to be able to design the optical band gap of an amorphous thin film freely by controlling directly the hydrogen content and hydrogen bond gestalt of an amorphous semiconductor thin film by repeating a membrane formation process and the process put to the hydrogen plasma, quality improvement of the thin film by reduction of a defect can be attained. And if it pulls, it can





produce and cheat out of improvement in the conversion efficiency of a thin film solar cell especially an open end electrical potential difference, and a curvilinear factor.

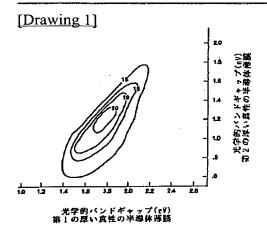
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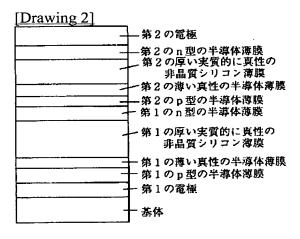
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#### **DRAWINGS**





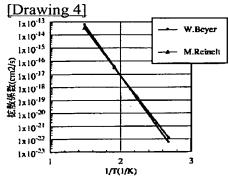


図4 非晶質シリコン薄膜中の水素原子 の拡散係数

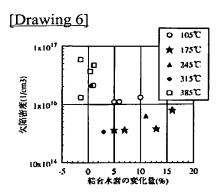


図6 結合水業の変化量と欠陥密度の関係

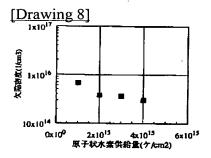


図8 原子状水素供給量と欠陥密度の関係

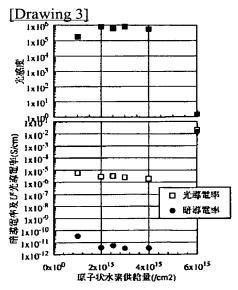
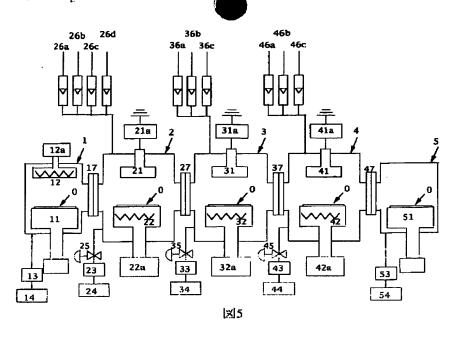


図3 原子状水素の供給量 と導電率及び光感度の変化

# [Drawing 5]



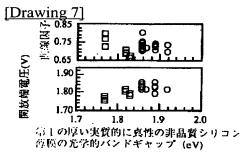
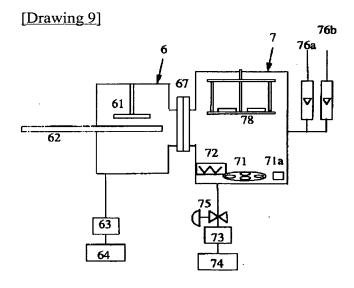


図7 水素希釈成膜法と本開示の方法の比較



[Translation done.]

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